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Structural Analysis Based on pMAIRS and GI-WAXD Methods for Thin Film Aromatic Polyimide Prepared from Liquid Crystalline Precursor

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Introduction

Recently, we synthesized a series of linear poly(amic ester)s (PAEs, **Fig. 1**), which is one of the precursors of aromatic polyimide (PI) and exhibits lyotropic liquid crystalline phase in a concentrated solution above 50 wt%. In this study, thin film structure of these PAEs and resultant PI were investigated by in-situ measurements based on synchrotron radiation wide-angle X-ray diffraction (SR-WAXD), and new spectroscopic method, variable temperature p-polarized multi-angle incidence resolution spectroscopy (VT-pMAIRS)[1] in the mid-infrared region, which provides in-plane and out-of-plane spectra separately at the same time in the same absorbance scale, and enables easy and precise molecular-orientation analysis for thin films.

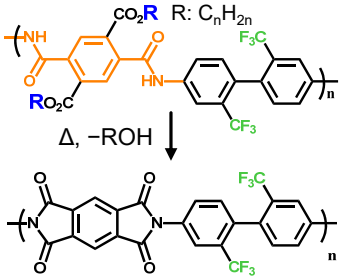

Fig. 1 Chemical structure of target PAE and resultant PI.

Experimental

Thin films of PAEs synthesized according to previous report[2] were spin-coated on Si wafers from diluted solutions. In-situ SR-WAXD measurements were conducted at BL-6A in Photon Factory (PF), High Energy Accelerator Energy Source (KEK), Tsukuba, Japan (Proposal No. 2015G587, 2016G544, and 2017G693). VT-pMAIRS measurements were conducted with FT/IR-6100FF (JASCO), which was equipped with AM-4000 rotation stage and home-made heating system.

Results and Discussion

The thin film of the PAE and resultant PI exhibited low planar orientation; uniaxial orientation order parameter, $S = (3\langle\cos^2\theta\rangle - 1)/2$, where θ is the angle between molecular axis and averaged orientation direction, was about −0.1 and −0.2 for the PAE and PI films respectively. Furthermore, the values of $|S|$ estimated by SR-WAXD were larger than those by pMAIRS, as shown in **Fig. 2**. This result implies that a heterogeneous structure containing non-oriented region was generated in the initial PAE film, because the PAE chains have shorter persistence lengths in the diluted solution, and then quenched by so fast evaporation of the solvent during spin-coating and a prebaking process that liquid-crystalline phase could not grow sufficiently.

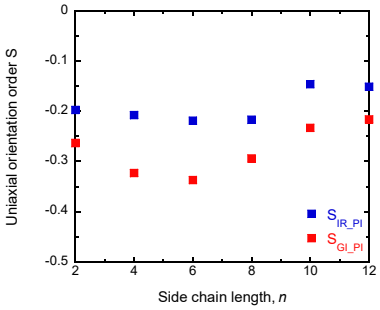

Fig. 2 Orientation order parameter S of a series of PAEs with different side chain length (blue) and resultant PI (red).

References

1) R. Ishige, K. Tanaka, S. Ando, *Macromol. Chem. Phys.*, **219**, 1700370 (2018).

2) C. Neuber, R. Giesa, H-W. Schmidt, *Macromol. Chem. Phys.*, **203**, 598 (2018).